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(54) Process for the production of  
aromatic polyesters

(57) The production of aromatic  
polyesters is facilitated by the

incorporation of a phosphite,  
particularly an organic phosphite,  
during the reaction procedure. Molded  
articles made from these polyesters  
have improved appearance and  
excellent properties.

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## SPECIFICATION

## Process for the production of aromatic polyesters

The present invention relates to an improved process for the production of aromatic polyesters. More particularly, it relates to a process for the production of oxybenzoyl polyesters of aromatic

dicarboxylic acids, bisphenols and p-hydroxybenzoic acid compounds as the starting materials. 5

It is known that aromatic polyester resins can be produced by various polymerization processes including suspension polymerization and bulk polymerization. Of these, the bulk polymerization process is perhaps the most desirable process in terms of economy. However, since aromatic polyesters have a high melting point as compared with aliphatic polyesters, such as polyethylene terephthalate, a higher temperature is required to maintain the aromatic polyesters in a molten state. Consequently, the polymers are often colored and deteriorated in performance. 10

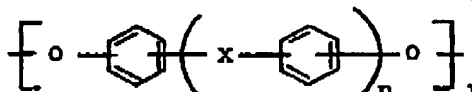
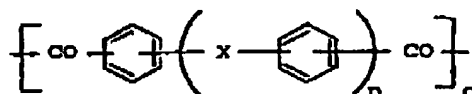
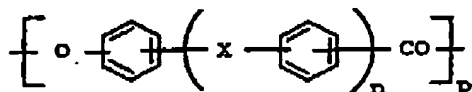
Much effort has therefore been expended on the development of a process which eliminates the disadvantages discussed above and provides a polyester molding material from which articles of pleasing and uniform appearance and properties can be obtained.

The invention provides a process for preparing an aromatic polyester which comprises the heat condensation of aromatic polyester precursors to form a prepolymer and thereafter advancing the prepolymer to form an aromatic polyester having the required degree of polymerization, wherein a phosphite compound is incorporated into the reaction procedure before completion of the polymerization. 15

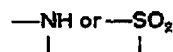
According to the present invention, there can be produced an aromatic polyester having an extremely low degree of coloration and an excellent heat stability which has hitherto not been obtainable by the conventional bulk polymerization. 20

Preferably the phosphite is added to the prepolymer melt prior to advancement of the final product to the desired degree of polymerization.

The wholly aromatic polyesters towards whose production the present invention is directed preferably contain, as recurrent moieties, at least one group selected from groups of the formulae: 25



30 where X is a direct bond, —O—, —S—, —CO—,



and n is 0 or 1 and the total of p+q+r+s+t+u in the moieties present is from 3 to 800.

Combinations of the above units include union of the carbonyl group of Formulae I, II, IV and V with the oxy group of Formulae I, III, IV and VI. In the most general combination units of all the above formulae can be present in a single copolymer. The simplest embodiment would be homopolymers consisting of units I or IV. Other combinations include mixtures of units II and III, II and VI, III and V, V and VI, and I and IV. 35

The functional groups attached to benzene rings are preferably in the para (1,4) positions, but can be located in meta (1,3) positions. With respect to the groups containing naphthalene rings, the most desirable locations of the functional groups are 1,4; 1,5 and 2,6, but the groups can also be in the meta position to each other. 40

The symbols p, q, r, s, t and u are 0 or integers and indicate the number of moieties present in the polymer. The total (p+q+r+s+t+u) can vary from 3 to 800 and, when present, the ratio of q/r, q/u, t/r, t/u,

45  $\frac{q+t}{r}$ ,  $\frac{q+t}{r+u}$  and  $\frac{t}{r+u}$  45

can vary from about 10/11 to about 11/10 with the most preferable ratio being 10/10.

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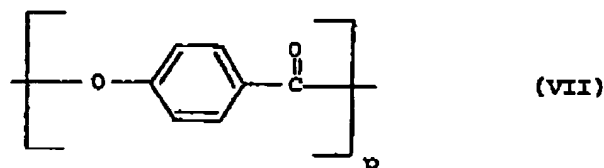
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Exemplary of materials from which the groups of Formula I may be obtained are p-hydroxybenzoic acid, phenyl p-hydroxybenzoate, p-acetoxybenzoic acid and isobutyl p-acetoxybenzoate. Monomers from which groups of Formula II are derivable include terephthalic acid, isophthalic acid, diphenyl terephthalate, diethyl isophthalate, methylethyl terephthalate and the isobutyl half ester of terephthalic acid. Among the compounds from which groups of Formula III result are p,p'-bisphenol; p,p'-oxybisphenol; 4,4'-dihydroxybenzophenone; resorcinol and hydroquinone.

Examples of monomers which yield groups represented by Formula IV are 6-hydroxy-1-naphthoic acid; 5-acetoxy-1-naphthoic acid and phenol 5-hydroxy-1-naphthoate. Monomers which yield groups represented by Formula V include 1,4-naphthalenedicarboxylic acid; 1,5-naphthalenedicarboxylic acid and 2,6-naphthalenedicarboxylic acid. The diphenyl esters or dicarbonyl chlorides of these acids can also be used. Examples of monomers which yield groups of Formula VI are 1,4-dihydroxynaphthalene; 2,6-diacetoxynaphthalene and 1,5-dihydroxynaphthalene.

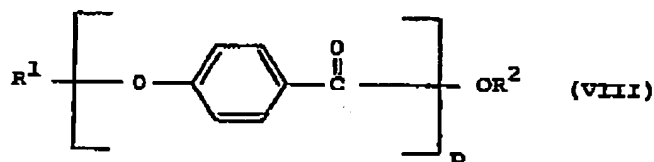
Particularly preferred for use in the practice of the present invention are monomers which yield oxybenzoyl polyesters.

The oxybenzoyl polyesters which may be prepared by the process of the present invention generally contain repeating units of Formula VII:



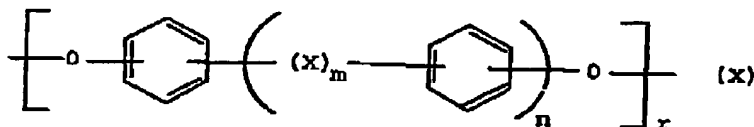
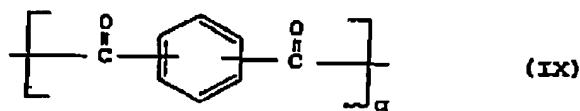
where p is an integer of from 3 to 600.

Preferred oxybenzoyl polyesters are those of Formula VIII:



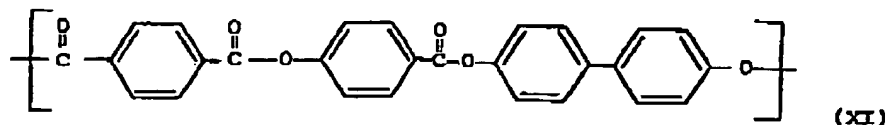
wherein R<sup>1</sup> is selected from benzoyl, lower alkanoyl, or preferably hydrogen; R<sup>2</sup> is hydrogen, benzyl, lower alkyl, or preferably phenyl; and p is an integer from 3 to 600 and preferably 30 to 200. These values of p correspond to a molecular weight of 1,000 to 72,000 and preferably 3,500 to 25,000. The synthesis of these polyesters is described in detail in U.S. Patent Application Serial No. 619,577, filed March 1, 1967, and now abandoned, entitled "Polyesters Based on Hydroxybenzoic Acids". This application is referred to in U.S. Patent No. 3,668,300.

Other preferred oxybenzoyl polyesters are copolyesters containing recurring units of Formulas VII, IX and X:



wherein X is —O— or —SO<sub>2</sub>—; m is 0 or 1; n is 0 or 1; q:r=10:15 to 15:10; p:q=1:100 to 100:1; p+q+r=3 to 600 and preferably 20 to 200. The carbonyl groups of the moiety of Formula VII or IX are linked to the oxy groups of a moiety of Formula VII or X; the oxy groups of the moiety of Formula VII or X are linked to the carbonyl groups of the moiety of Formula VII or IX.

The preferred copolyesters are those containing recurring units of Formula XI:



The synthesis of these polyesters is described in detail in U.S. Patent No. 3,637,595, entitled "P-Oxybenzoyl Copolyesters".

The bulk condensation of aromatic polyesters is described in the patent literature and broadly considered involves an alkanoylation step, for example by reacting a dicarboxylic acid, hydroxybenzoic acid and a diol in the presence of an acid anhydride, a prepolymerization step in which the reaction product of the first step is polycondensed to prepare a prepolymer and a polymerization step in which the prepolymer is heated to produce a polycondensate having the desired degree of polymerization.

The polyesters useful in the present invention can also be chemically modified by various means such as by inclusion in the polyester of monofunctional reactants such as benzoic acid or tri- or higher functional reactants such as trimesic acid or cyanuric chloride. The benzene rings in these polyesters are preferably unsubstituted but can be substituted with non-interfering substituents, examples of which include halogen such as chlorine or bromine, lower alkoxy such as methoxy and lower alkyl such as methyl.

The phosphite can be an organic or inorganic phosphite. However, the use of an organic phosphite, such as an alkyl phosphite, an aryl phosphite, an alkyl-aryl phosphite or a di- or polyphosphite is preferred. Examples of phosphites which can be employed are diisooctyl phosphite, distearyl phosphite (solid), trisodecyl phosphite, triisooctyl phosphite, trilauryl phosphite, diphenyl phosphite, trisonylphenyl phosphite, triphenyl phosphite, diphenylisodecyl phosphite, diphenylisooctyl phosphite, phenyldisodecyl phosphite, diisodecyl pentaerythritol diphosphite, tetraphenyl dipropyleneglycol diphosphite, poly(dipropyleneglycol) phenyl phosphite, dilauryl phosphite, ethyl hexyl diphenyl phosphite, phenyl neopentylglycol phosphite, diisooctyl octylphenyl phosphite and distearyl pentaerythritol diphosphite (flake).

While the phosphite can be added at any stage of the reaction procedure, it has been found to be particularly effective, and to provide markedly superior properties in the articles molded from the aromatic polyester resin, if the phosphite is added shortly before, for example above five minutes before, the prepolymer is transferred to the next stage, as by dumping into an insulated tray wherein an intermediate stage of polymerization takes place before the resin is transferred to suitable equipment, for example a rotary heating drum, for advancement to the desired stage of polymerization.

In another approach to the determination of the optimum point for addition of the phosphite, it has been found that the phosphite can most advantageously be added at about 95% conversion as indicated by the distillate yield of acetic acid.

The phosphite can be added as solid flakes or as a liquid melt at a temperature above the melting point of the phosphite. It is also possible to add the phosphite in a solution in acetic anhydride when incorporation is effected at a lower temperature. Addition in melt form is in general preferred.

The amount of phosphite added is dependent on the purity of the monomer. The purer the monomer, the less phosphite need be added to achieve the desired result. The purity is related to the phenol and the amount of phenol employed and to the amount of ash produced. Where there is a higher ash content, increased amounts of phosphite will be required to achieve optimum results, which requires a balancing of the achievement of the optimum levels for the achievement of optimum results in achieving the desired color and the desired level of thermal stability.

Broadly, the phosphite has been added over a range of from about 0.05 parts by weight per hundred parts by weight of resin (phr) to about 0.5 phr, preferably about 0.1 to 0.25 phr, with 0.125 phr representing the optimum proportion.

The invention will be illustrated further by reference to the following Examples, in which Example 1 provides a control in which no phosphite is added.

#### Example 1 (control)

A charge of 207.3 g (1.096 moles) of 4,4'-dihydroxybiphenyl (Assay 98.5%), 307.6 g (2.23 moles) of 4-hydroxybenzoic acid, 185 g (1.11 moles) of terephthalic acid and 498 g (4.88 moles, 10% excess) of acetic anhydride was refluxed with stirring for three hours. The contents of the reactor were then blanketed with nitrogen and the mixture heated at an average rate of 30°C/hr to 295°C and held for one-half hour at this temperature. At this point, the reaction mixture was dumped into a "Pyrex" (Registered Trade Mark) dish lined with aluminium foil and the resulting prepolymer ground and passed through a 20 mesh screen.

The prepolymer (5.484 g) was inserted into a tube furnace already preheated to 229°C. With a slight nitrogen sweep the temperature of the material was raised to 360°C in four hours and held at 360°C for one hour.

After cooling, the material was weighed and the weight loss from prepolymer to advanced polymer was found to be 3.6%. This polymer showed a peak endotherm at 417°C as determined by differential scanning calorimetry (DSC) under nitrogen. The resin showed a total weight loss in air of 3.6% when heated at 400°C for three hours using thermogravimetric analysis (TGA). The rate of weight loss at 400°C in air was 1.2%/hr after the first hour.

Example 2 illustrates the effect of the addition of 0.28 pph of distearyl pentaerythritol diphosphite to prepolymer melt before dump.

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**Example 2**

The charge and process were the same as in Example 1 except that at a point five minutes prior to the prepolymer dump, 1.75 g (0.28 pph based on theoretical advanced polymer yield) of distearyl pentaerythritol diphosphite was added to the prepolymer melt.

5 This prepolymer, after grinding and screening, was also advanced under a nitrogen sweep by the process described in Example 1. This time, the weight loss from 6.184 g of the prepolymer was found to be 5.17% from prepolymer to advanced polymer. The peak endotherm by differential scanning calorimetry was found to be at 410°C. The weight loss of this resin as determined by TGA was only 0.7% after three hours at 400°C in air. The rate of weight loss after the first hour was only 0.2%/hr compared to 1.2%/hr as with the control sample.

10 Examples 3 and 4 compare the results obtained without (Example 3) and with (Example 4) addition of distearyl pentaerythritol diphosphite to prepolymer in a rotary drum prior to advancing.

**Example 3 (control)**

15 A mixture of 301.1 g (2.18 moles) of 4-hydroxybenzoic acid, 181.08 g (1.09 moles) of terephthalic acid, 203.88 g (1.09 moles, Assay 99.5%) of 4,4'-dihydroxybiphenyl and 526 g (5.15 moles, 18% excess) of acetic anhydride was refluxed for four hours. Under a nitrogen blanket, the mixture was heated at a rate of 40°C/hr until 97.2% of the total theoretical distillate (including excess anhydride) was obtained. At this point the temperature in the reactor had reached 340°C. The contents of the reactor were dumped into an aluminum pan, allowed to cool and ground in a Wiley Mill through a 1 mm screen. A yield of 803 g was obtained.

20 This prepolymer was then advanced without addition of distearyl pentaerythritol diphosphite in a rotary drum.

A total of 200 g of the prepolymer was placed in the rotary drum and heated at a rate of 44°C/hr under a nitrogen sweep of 6 SCFH and a rotation of 15 rpm. When the temperature of the resin reached 354°C, the material was held at 354°C for one hour and then cooled rapidly. The yield of advanced polymer was 96%. The resin had a peak endotherm at 420°C and showed a weight loss in air of 0.84% at 400°C after three hours (TGA). The rate of weight loss was 0.18%/hr after the first hour.

**Example 4**

30 A mixture of 200 g of prepolymer obtained as described in Example 3 and 0.5 g (0.250 pph) of distearyl pentaerythritol diphosphite was placed in a rotary drum and advanced as described in Example 3. The yield of advanced polymer from prepolymer was 96.5%. This advanced resin had a peak endotherm at 421°C (differential scanning calorimetry). The total weight loss at 400°C in air after three hours was 0.87% with a rate of weight loss of 0.14%/hr after the first hour.

35 Example 5 illustrates the effect of adding 0.125 pph distearyl pentaerythritol diphosphite to a prepolymer melt at 95% conversion.

**Example 5**

40 The charge and the process was the same as in Example 3 except that when the total distillate yield was 95% of theoretical (including excess acetic anhydride), 0.81 g (0.125 pph based on theoretical polymer weight) of distearyl pentaerythritol diphosphite was added. (The temperature of the melt was 330°C at this point). The mixture was heated further to 340°C in 15 minutes and the reactor content dumped into an aluminum pan. A total distillate yield of 588 g (97.4% of theoretical including excess acetic anhydride) was obtained and the prepolymer yield was 590 g.

45 After grinding and screening of the prepolymer as in Example 3, 200 g was charged in a rotary drum and advanced to 354°C and held one hour (as in Example 3). The resulting advanced polymer had a reversible first peak endotherm at 421°C (differential scanning calorimetry). Total weight loss in air after three hours at 400°C (TGA) was 0.75% with a rate of weight loss of 0.08%/hr after the first hour. This represents a 2.25% fold decrease in the rate of weight loss over the unstabilized polymer and a 1.75% fold decrease over that of resin prepared with twice as much distearyl pentaerythritol diphosphite added to the drum.

**Example 6**

55 The charge and the process were the same as in Example 5 for each of the additives and additive levels shown in the Table below. The differences between additives and additive levels was the only variation from the procedure of Example 5. The additives were introduced at the point at which the total distillate yield was 95% of theoretical (including excess acetic anhydride). The relative weight loss determined is set forth in the Table.

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Table  
Other phosphite additives and levels<sup>1</sup>

5	Phosphite	pph <sup>2</sup>	Relative rate <sup>3</sup> of weight loss 400°C, air	5
	Distearyl Pentaerythritol Diphosphite	0.00 0.10 0.125 0.250	3.8 1.2 1.0 1.8	
10	Trisnonylphenyl Phosphite	0.125 0.250	1.05 1.83	10
	Bis(2,4-DI-t-Butylphenyl) Pentaerythritol Diphosphite	0.125 0.250	1.0 1.2	
15	Diisodecyl Pentaerythritol Diphosphite Triphenyl Phosphite	0.125 0.250 0.125	1.2 1.2 1.5	15

<sup>1</sup>In addition to optimum level of phosphite regarding rate of weight loss, too much or too little phosphite additive can affect the color and homogeneity. The above examples are based on high purity-low ash monomers.

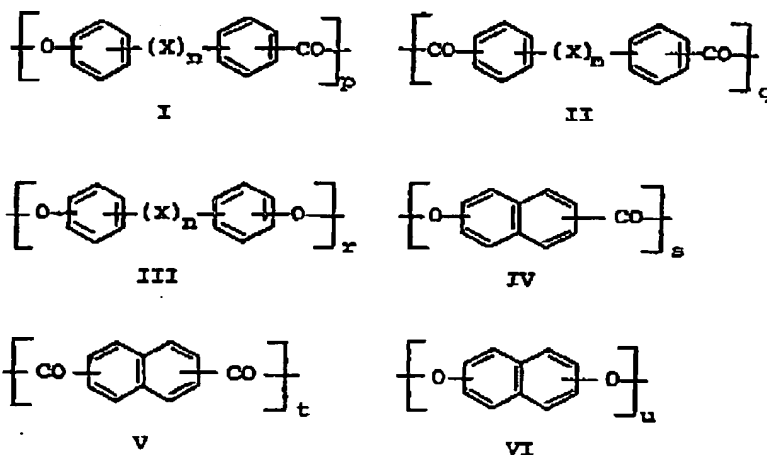
<sup>2</sup>Base on phosphorus content to give equivalent pph of distearyl pentaerythritol diphosphite.

<sup>3</sup>Relative rate of weight loss of advanced resin compared to advanced resin using 0.125 of distearyl pentaerythritol diphosphite giving 1.0 rate of weight loss as the standard.

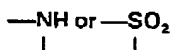
#### Claims

25 1. A process for preparing an aromatic polyester which comprises the heat condensation of aromatic polyester precursors to form a prepolymer and thereafter advancing the prepolymer to form an aromatic polyester having the required degree of polymerization, wherein a phosphite compound is incorporated into the reaction procedure before completion of the polymerization.

30 2. A process according to claim 1, wherein the polyester contains, as recurring moieties, at least one group selected from groups of the formulae:



where X is —O—, —S—, —CO—,



and n is 0 or 1 and the total of p+q+r+s+t+u in the moieties present is from 3 to 800.

3. A process according to claim 1 or 2, wherein the phosphite compound is an organic phosphite.

4. A process according to claim 3, wherein the phosphite compound is distearyl pentaerythritol diphosphite.

40 5. A process according to any one of the preceding claims, wherein the addition of the phosphite compound takes place shortly before transfer of the prepolymer to the polymerization stage.

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6. A process according to any one of claims 1 to 4, wherein the addition of the phosphite compound takes place at the point of 95% conversion.

7. A process according to claim 1 substantially as described in Example 2, 4, 5 or 6.

8. Molded articles of an aromatic polyester prepared by a process as claimed in any one of the preceding claims.

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